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SOLVENT EXTRACTION REMOVAL OF Fe(III) FROM INDUSTRIAL ACIDIC SOLUTIONS

P.J.A. Prud'homme, G. Pouskouleli
Extractive Metallurgy Laboratory

G.P. Demopoulos
McGill University

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SOLVENT EXTRACTION REMOVAL OF Fe(III) FROM INDUSTRIAL ACIDIC SOLUTION

by

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ABSTRACT

The ability of mono-2-ethylhexyl phosphoric acid (M2EHPA)* to remove ferric iron from industrial sulphuric acid solutions was studied. The extractant was able to selectively extract iron in the presence of other metals such as Zn, Cu, Bi, Ag, etc., over a large range of H_2SO_4 concentrations without any need for pH control, thus outperforming other cationic extractants previously investigated, i.e., Versatic acid, D2EHPA. Stripping of the Fe(III)-loaded extractant was accomplished with strong HCl solutions. This new solvent extraction system appears to offer a convincing alternative to the present iron precipitation methods used by the zinc industry (i.e., jarosite, goethite, hematite) and warrants further progress development work.

Keywords: iron, removal, extraction, purification, sulphate, monophosphoric acid.

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* Mono-2-ethylhexyl phosphoric acid (LPKN 191 manufactured by Hoechst)

EXTRACTION DU MINERAI DE FER, FE(III), DES SOLUTIONS INDUSTRIELLES ACIDES AU MOYEN D'UN SOLVANT D'EXTRACTION

par

P.J.A. Prud'homme, G. Pouskouleli, G. Demopoulos

RÉSUMÉ

On a étudié les capacités de l'acide mono-2-éthylhexyl phosphorique pour extraire le Fe(III) contenu dans des solutions industrielles d'acide sulfurique. Le solvant d'extraction a pu faire une extraction sélective du fer en présence d'autres métaux tels, le zinc (Zn), le cuivre (Cu), le bismuth (Bi), l'argent (Ag), etc. L'extraction du fer d'une large gamme de concentrations de H_2SO_4 a été effectuée de cette façon sans qu'aucun contrôle du pH n'ait été nécessaire. Le rendement du solvant d'extraction a surpassé celui d'autres solvants d'extraction cationiques qui avaient fait l'objet d'études antérieures, notamment l'acide Versatic, D2EHPA. Le décapage du solvant d'extraction à forte teneur en Fe(III) a été effectué au moyen de solutions de HCl très fortes. Cette nouvelle technique d'extraction semble présenter une alternative intéressante aux méthodes de précipitation du fer utilisées par l'industrie du zinc. (i.e., la jarosite, la géothite, l'hématite). D'autres recherches seront nécessaires afin de développer la technique.

Mots-clé : fer, extraction, épuration, sulfate, acide monophosphorique

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* Acide mono-2-éthylhexyl phosphorique (LPKN 191, fabriqué par Hoechst)

INTRODUCTION

A report of invention was recently filed for a new extraction system for removal of Fe(III) from hot acid zinc leach solutions without pH control[1]. In this present paper the technical work which led to this report of invention is described and technical data are reported. The basis of this work is that the extractant mono-2-ethylhexyl phosphoric acid (M2EHPA) selectively extracts Fe(III) from H_2SO_4 acid solutions. In the past, other investigators have advanced the use of Versatic acid and/or D2EHPA extractants for the removal of Fe(III). Our extraction system, having better characteristics since it works in a pH control-free system, appears very attractive for the Zn industry. At the same time it may solve an environmental problem which is created with the disposal of the precipitated iron jarosite as industry is now doing. Furthermore, losses of valuable metals, e.g., Zn, Ag, in the jarosite are also eliminated.

This report gives technical data for extracting and stripping of Fe(III) from electrolyte solutions, both real and synthetic.

EXPERIMENTAL

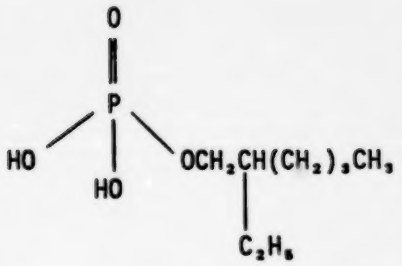
The extractant (M2EHPA), obtained from Hoechst under the trade name LPKN 191, was used as either 18.3 or 25 v/o solution with 26.7 or 25 v/o isodecanol in Varsol 140 (aliphatic diluent).

The aqueous solutions used were either made up synthetically using "chemically pure" grade sulfate salts or they were samples of industrial solutions received from Canadian Copper Refinery (CCR) and Kidd Creek Mines Ltd.

All the extraction shake-out tests were carried out in separatory funnels at room temperature. Stripping of the loaded organic was performed with two agents, sulfuric acid and hydrochloric acid. Metal values in aqueous and organic phases were analysed by AA using standard procedures.

RESULTS AND DISCUSSION

Mono-2-ethylhexyl phosphoric acid (M2EHPA) belongs to a class of extractants which extract hard metallic ions, e.g., iron (III).



Kinetics Studies

M2EHPA was found to extract iron from acidic sulfate liquors of various activities. The extraction kinetics are fast with more than >-98.8% of the iron extracted within a retention time of 2-20 min. at an acidity level of 21.1 kg H_2SO_4/m^3, while between 87-88% was extracted at 154 kg H_2SO_4/m^3 (Table 1). Retention time seemed to have no effect on iron extraction but the latter is greatly affected by the acidity level.

Table 1. Effect of acidity level and retention time (RT) on Fe(III) extraction

	Distribution Coefficient (D)		% Extraction	
RT(min)	21.1 kg H_2SO_4/m^3	154 kg H_2SO_4/m^3	21.1 kg H_2SO_4/m^3	154 kg H_2SO_4/m^3
2	83.0	7.1	98.8	87.7
5	92.3	7.5	98.9	87.2
10	91.4	7.3	98.9	88.0
15	91.4	7.1	98.9	87.7
20	91.4	6.9	98.9	87.3

* A/O = 1, T = 24°C, AF = 8.92-9.24 kg Fe^T/m^3, 0.001-0.012 kg Fe^{2+}/m^3, ORG = 18.3 v/o (M2EHPA) + 26.7 v/o isodecanol in Varsol 140.

An increase of acidity level in the raffinates was noticed, (with aqueous feed solutions of 21.1 and 154 kg H_2SO_4/m^3 raffinates were respectively ≈ 54 and ≈ 181 kg H_2SO_4/m^3) which is due to the following acidity dependent reactions taking place during the extraction:

$$Fe_2(SO_4)_3 + 3M2EHPA \longrightarrow Fe_2(M2EHP)_3 + 3H_2SO_4$$

$$Fe_2(SO_4)_3 + 6\ M2EHPA \longrightarrow 2[Fe\ (M2EHP)_3] + 3H_2SO_4$$

The effect of lower acidity levels on iron extraction was also studied with 25 v/o (M2EHPA) and it showed that at lower acidity levels an increase in acidity from 22 to 64 kg H_2SO_4/m^3, resulted in only a slight decrease in iron extraction from 51.0% to 47.4% (Table 2).

Table 2. Effect of acidity level on Fe(III) extraction

Acidity level kg H_2SO_4/m^3		D Fe^{+3}	% Fe^{+3} ext
(Feed)	(RAF.)		
21.9	63.1	2.08	51.0
47.2	94.9	1.95	49.4
64.2	122.0	1.80	47.4

* A/O = 2, T = 24°C, Rt= 1 min., AF = 18.6-19.3 kg Fe^T/m^3, 0.015 Fe^{2+}/m^3, ORG = 25% (M2EHPA) + 25% isodecanol in Varsol 140.

Other tests were done to determine the effect of extractant (M2EHPA) concentration as well as the effect of iron concentration on iron extraction.

Table 3. Effect of M2EHPA concentration on distribution coefficient

Acidity level Kg H_2SO_4/m^3		[M2EHPA] v/o	D Fe^{+3}	% Fe^{+3} ext
(Feed)	(RAF.)			
49.4	73.2	6	0.39	28.3
36.8	75.2	12	1.07	51.6
27.5	73.8	18.3	2.09	67.6
20.7	74.9	24	3.86	79.4

* A/O = 1, T = 24°C, RT = 5 min., AF 18.3-19.0 kg Fe^T/m^3, 0.023-0.030 kg Fe^{2+}/m^3, ORG = [M2EHPA] + 26.7 v/o isodecanol in Varsol 140.

Table 4. Effect of iron concentration in feed solution on Fe(III) extraction

Acidity level Kg H_2SO_4/m^3		Kg Fe^{+3}/m^3	D Fe^{+3}	% Fe^{+3} ext
(Feed)	(RAF.)	(Feed)		
40.5	59.4	5.19	246.14	99.6
19.9	70.0	13.7	4.55	82.0
21.5	86.7	31.3	1.41	58.5

* A/O = 1, T = 24°C, RT = 5 min., AF = 0.007-0.052 Fe^{+2}/m^3, ORG = 18.3% (M2EHPA) + 26.7% isodecanol in Varsol 140.

Extraction of H_2SO_4 by M2EHPA has been studied. The results are inconclusive at this point. Solubility tests will have to be performed to examine the extent of M2EHPA transfer to the aqueous phase.

Table 5. H_2SO_4 extraction by M2EHPA

RT (min.)	Acidity Levels Kg H_2SO_4/m^3	
	Feed	RAF.
1	50.2	59.0
5	50.2	61.0
10	50.2	62.1
15	50.2	67.8

A/O = 1, T = 24°C, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140.

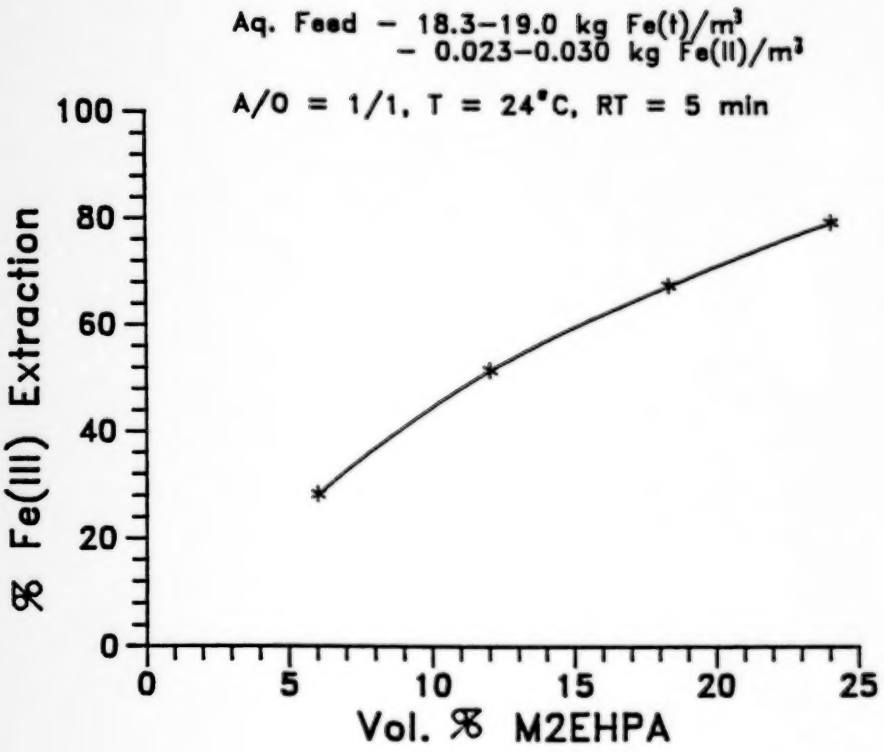


Fig. 1. The effect of [M2EHPA] on iron extraction (RT = 5 min.)

A kinetic test on exchange extraction has been done to show that zinc can be displaced from a loaded organic by iron thus indicating the selectivity of the extractant for iron over zinc. A solution containing 26.4 kg Zn/m³ at a pH of 3.78 was contacted with the extractant (18.3 v/o M2EHPA) for 5 min. at room temperature and A/O = 2. Zinc extraction achieved was 11.4% giving a loaded organic containing 6 kg Zn/m³. This remaining loaded organic was contacted for 1, 5, 10 and 15 min. retention times with an iron solution containing 8.99 kg Fe^{+3}/m³ at an acidity level of 60.2 kg H_2SO_4/m³. The results are shown in Table 6.

Table 6. Effect of retention time (RT) on exchange extraction

Acidity level
kg H_2SO_4/m^3

(Feed)	(RAF.)	RT(min)	D Fe^{+3}	D Zn	% Fe^{+3} ext	% Zn stripping
60.2	71.2	1	28.0	10.61×10^{-3}	96.6	99.0
60.2	73.0	5	151.4	2.67×10^{-3}	99.3	99.7
60.2	71.6	10	159.5	3.01×10^{-3}	99.4	99.7
60.2	72.0	15	168.6	1.34×10^{-3}	99.4	99.9

* A/O = 1, T = 24°C, AF = 8.99 kg Fe^{+3}/m^3, 0.011 kg Fe^{+2}/m^3, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140, ORG loading = 6 kg Zn/m^3

Some more kinetic studies were done at different acidity levels with synthetic aqueous feed solutions containing iron (III), copper, bismuth and zinc as well as with a spent electrolyte solution obtained from Canadian Copper Refinery (CCR) to which silver had been added. Results showed that iron (III) is preferentially extracted over copper and zinc at acidities ranging from ≈20 to 155 kg H_2SO_4/m^3, and that, at the same time, iron (III) is preferentially extracted over bismuth only at an acidity level of 155 kg H_2SO_4/m^3. Retention time did not seem to have much effect on iron (III) extractions which is not always the case for bismuth extraction. An increase of the acidity level from ≈20 to 155 kg H_2SO_4/m^3 resulted in a decrease of iron (III) extraction from ≈99% to 81-87%. At ≈154 kg H_2SO_4/m^3 when silver and antimony are present, 7.1% to 49.3% of the silver and 31.3% to 37.5% of the antimony are extracted respectively in the 1 and 20 min. retention time.

The obtained results are summarized in Tables 7, 8, 9, 10.

Aqueous solution compositions were as follows (in kg/m^3):

Synthetic feed solution				CCR feed solution			
Fe^T	8.15-8.97	Zn	9.50-9.62	Fe^T	0.58		
Fe^{2+}	<0.001			Fe^{2+}	<0.001	Ag	0.14
Fe^{3+}	8.15-8.97			Fe^{3+}	0.58	As	1.62
Cu	8.32-9.26			Cu	42.9	Sb	0.16
Bi	0.46-0.50	H_2SO_4	19-155	Bi	0.21	H_2SO_4	154

Table 7. Effect of acidity level and retention time (RT) on metal extraction by M2EHPA from synthetic solutions

Acidity Level (AF)	(H_2SO_4 kg/m³) (RAF.)	RT(min.)	D Fe^T	D Cu	D Bi	D Zn	% Fe^{+3} ext.	% Bi ext.
19.3	51.3	1	99	0.08	166	0.063	99.0	99.4
	50.0	5	99				99.0	
	51.5	15	101		62		99.0	
	51.6	20	99	0.09		0.015	99.0	98.4
47.5	81.1	1	29	nil	15	nil	96.7	93.8
	80.4	5	32				96.9	
	78.0	15	34		11	nil	97.2	
	80.2	20	33				97.1	91.5
73.3	103	1	16	0.02	5.4	nil	94.0	84.5
	103	5	20				95.2	
	102	15	19				95.0	
	104	20	19	0.01	2.6	nil	95.0	72.3
99.1	129	1	11	0.01	2.1	nil	91.4	67.4
	126	5	12				92.4	
	126	15	12				92.4	
	133	20	13	0.006	0.9	nil	92.7	47.8
155	179	1	4	nil	0.07	0.021	81.2	6.5
	177	5	7				87.1	
	179	15	7				87.4	
	181	20	7	nil	0.10	nil	87.5	8.7

A/O = 1, T = 24°C, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140.

Table 8. Effect of acidity level and retention time (RT) on selectivity of Fe(III) extraction

Acidity Level (H_2SO_4 kg/m³)	(H_2SO_4 kg/m³) (RAF.)	RT(min.)	Fe^{+3}/Cu	Fe^{+3}/Bi	Fe^{+3}/Zn	% Fe^{+3} ext.
19.3	51.3	1	1238	0.60	1571	99.0
	50.0	5				99.0
	51.5	15				99.0
	51.6	20	1100	1.60	6600	99.0
47.5	81.1	1	-			96.7
	80.4	5		1.93		96.9
	78.0	15				97.2
	80.2	20	-	3		97.1
73.3	103	1	800	2.96		94.0
	103	5				95.2
	102	15				95.0
	104	20	1900	7.31		95.0
99.1	129	1	1100	5.24		91.4
	126	5				92.4
	126	15				92.4
	133	20	2167	14.44		92.7
155	179	1	-	57.14	190	81.2
	177	5				87.1
	179	15				87.4
	181	20	-	70.00		87.5

A/O = 1, T = 24°C, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140

Table 9. Effect of retention time (RT) on metal extraction from CCR spent electrolyte solutions

Acidity Level	(AF)	154	154	154	154
(H_2SO_4 kg/m³)	(RAF.)	172	167	164	170
Retention time (min.)		1	5	15	20
D Fe^{+3}		4	8	10	10
D Ag		0.08	-	-	0.97
D Bi		0.11	-	-	0.11
D Sb		0.45	-	-	0.45
D As		0.013	-	-	0.013
D Cu		nil	-	-	nil
% Fe^{+3} extr.		81.0	89.1	90.7	90.5
% Ag extr.		7.1	-	-	49.3
% Bi extr.		9.5	-	-	9.5
% Sb extr.		31.3	-	-	37.5
% As ext.		1.2	-	-	1.2

Contacts at A/O=1, T=24°C
ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140.

Table 10. Effect of retention time (RT) on selectivity of Fe(III) extraction from CCR spent electrolyte solution

RT(min.)	Fe^{+3}/Ag	Fe^{+3}/Bi	Fe^{+3}/Sb	Fe^{+3}/As	Fe^{+3}/Cu	%Fe^{+3} extr.
1	50	36	8.9	307.7		81.0
5						89.1
15						90.7
20	10	91	16.7	769.2		90.5

A/O = 1, T = 24°C, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140

Equilibrium and Maximum Loading

Extraction isotherms at room temperature were obtained with two different concentrations of M2EHPA, 18.3 v/o and 25 v/o with 5 and 1 min. retention time respectively.

The results are summarized in Tables 11 and 12 and Fig. 2.

Table 11. Effect of A/O ratios on iron and zinc extraction

A/O	D Fe^{+3}	D Zn	D Fe^{+3}/Zn	% Fe^{+3} extr.	% Zn extr.
1/1	7.69	194.0×10^{-4}	396.4	88.5	1.90
2/1	2.49	665.7×10^{-4}	37.4	55.5	3.22
3/1	1.93	400.6×10^{-4}	48.2	39.2	1.32
5/1	1.69	-	-	25.3	-
7/1	1.48	-	-	17.5	-
1/2	29.14	29.5×10^{-4}	>9800	98.3	0.59
1/3	24.82	44.5×10^{-4}	>5500	98.7	1.32

AF(Kidd Creek) 16.6 kg Fe^{+3}/m^3, 0.075 kg Fe^{2+}/m^3, 68.3 kg Zn/m^3, 41.1 kg H_2SO_4/m^3, ORG = 25 v/o M2EHPA + 25 v/o isodecanol in Varsol 140, RT=1 min.

Table 12. Effect of A/O ratio on iron extraction

A/O	D Fe^{+3}	% Fe^{+3} extr.
2/1	6.65	76.9
5/1	3.32	39.9
10/1	2.66	21.0
1/2	152.33	99.6
1/5	31.38	99.4
1/10	4.27	97.7

AF = 8.45-9.17 kg Fe^{+3}/m^3, 0.011-0.016 kg Fe^{2+}/m^3, 26.4 kg H_2SO_4/m^3, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140, RT=5 min.

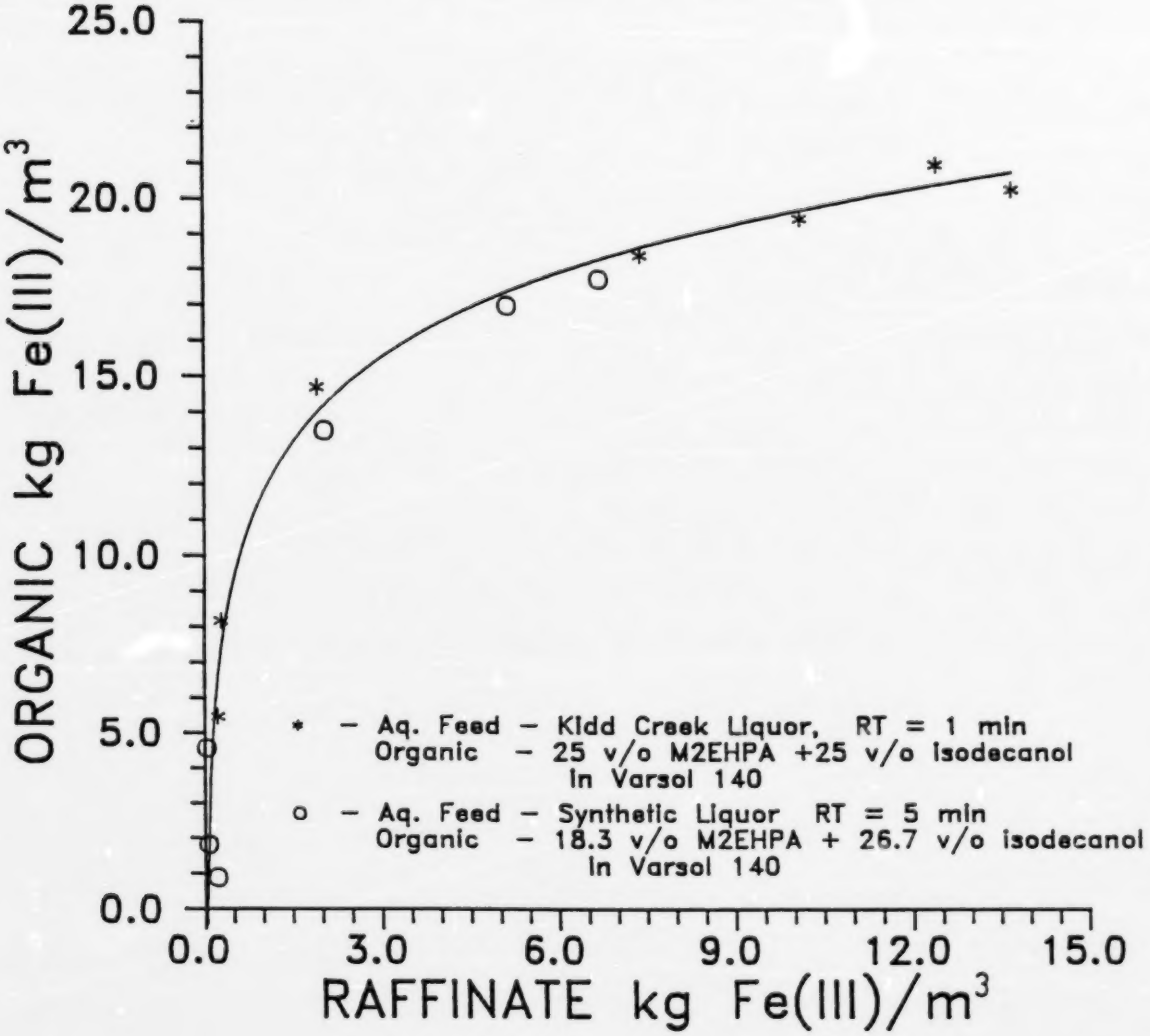


Fig. 2. Extraction isotherms

Stripping Studies

In order to select a stripping agent, screening tests were performed with two possible agents, sulfuric acid and hydrochloric acid. One concentration of H_2SO_4 and various concentrations of HCl were tested, i.e., 1, 3, 5 N at room temperature; also 5 N HCl has been tested at a temperature of 45°C. Best results (64% iron stripping) were achieved with 5 N HCl at 45°C and a retention time of 20 min (Table 13).

Table 13. Effect of retention time (RT) and stripping agent on stripping of Fe(III) from loaded M2EHPA organic solvents

Stripping agent	RT(min)	T°C	D Fe^{+3}	% Stripping efficiency
3 M H_2SO4^{+}	1	24	0.149	13.0
3 M H_2SO4	5	24	0.259	20.6
3 M H_2SO4	15	24	0.259	20.6
3 M H_2SO4	20	24	0.262	20.8
1 N HCl^{++}	20	24	-	0.62
3 N HCl	20	24	0.253	20.2
5 N HCl	20	24	1.333	57.1
5 N HCl	20	45	1.751	63.7

A/O = 1, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140, ORG loading $^{+}$ ≈8.14 kg Fe^{+3}/m^3, $^{++}$ ≈8.75 kg Fe^{+3}/m^3

The above data shows that retention time does not seem to have a major effect on iron stripping when 3 M H_2SO_4 is used. However HCl concentration has a major effect on iron stripping and higher temperature seems to favour stripping as well. Additional work has been done using 8 N HCl at 24°C and 45°C.

Results are shown in Table 14.

Table 14. Effect of retention time (RT) and temperature on stripping of Fe(III) from loaded M2EHPA organic solvent

Stripping agent	RT (min.)	D Fe^{T} 24°C	D Fe^{T} 45°C	% stripping 24°C	% stripping 45°C
8 N HCl	1	1.042	0.751	51.1	42.8
8 N HCl	3	1.042	0.709	51.1	41.6
8 N HCl	5	0.190	0.699	49.4	41.2
8 N HCl	10	0.920	0.694	49.1	41.0
8 N HCl	15	1.075	0.680	51.8	40.5
8 N HCl	30	0.970	0.704	49.2	41.4

O/A = 1, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140, ORG, loading 14.1 kg Fe^{+3}/m^3

Stripping of the loaded organic with mixtures of 6 N H_2SO_4, 0.25 M Na_2SO_3 and 6 N HCl, 0.25 M Na_2SO_3 were also examined. The results (Table 15) indicated that the presence of Na_2SO_3 in the H_2SO_4 acid solution did not improve the stripping while it did when HCl was used.

Table 15. Effect of Na_2SO_3 on stripping of loaded organic

Stripping agent	RT (min)	T°C	% stripping efficiency	D Fe^{+3}
3 M H_2SO_4 + 0.25 M Na_2SO_3	1	24	14.4	0.168
3 M H_2SO_4 + 0.25 M Na_2SO_3	10	24	20.4	0.256
3 M H_2SO_4 + 0.25 M Na_2SO_3	30	24	22.7	0.295
3 M H_2SO_4 + 0.25 M Na_2SO_3	60	24	23.4	0.305
6 N HCl + 0.25 M Na_2SO_3	1	24	56.7	1.307
6 N HCl + 0.25 M Na_2SO_3	10	24	59.6	1.478
6 N HCl + 0.25 M Na_2SO_3	10	47	69.4	2.264
6 N HCl + 0.25 M Na_2SO_3	30	24	61.2	1.579
6 N HCl + 0.25 M Na_2SO_3	60	24	61.6	1.606

Raising the temperature resulted in a considerable increase in the stripping efficiency as has been demonstrated previously.

Stripping Isotherm

A preliminary stripping isotherm was obtained with 8 N HCl at a retention time of 15 min. at room temperature. The results are summarized in Table 16 and Fig. 3.

Table 16. Effect of O/A ratios on Fe(III) stripping

O/A	D Fe^{+3}	% stripping
10/1	3.38	25.3
5/1	2.70	34.9
2/1	1.89	48.6
1/1	0.96	48.9
1/2	0.68	57.6
1/5	0.35	63.5
1/10	0.33	76.6

T = 24°C, RT = 15 min., stripping agent 8 N HCl, ORG = 18.3 v/o M2EHPA + 26.7 v/o isodecanol in Varsol 140, ORG loading 14.1 kg Fe^{+3}/m^3

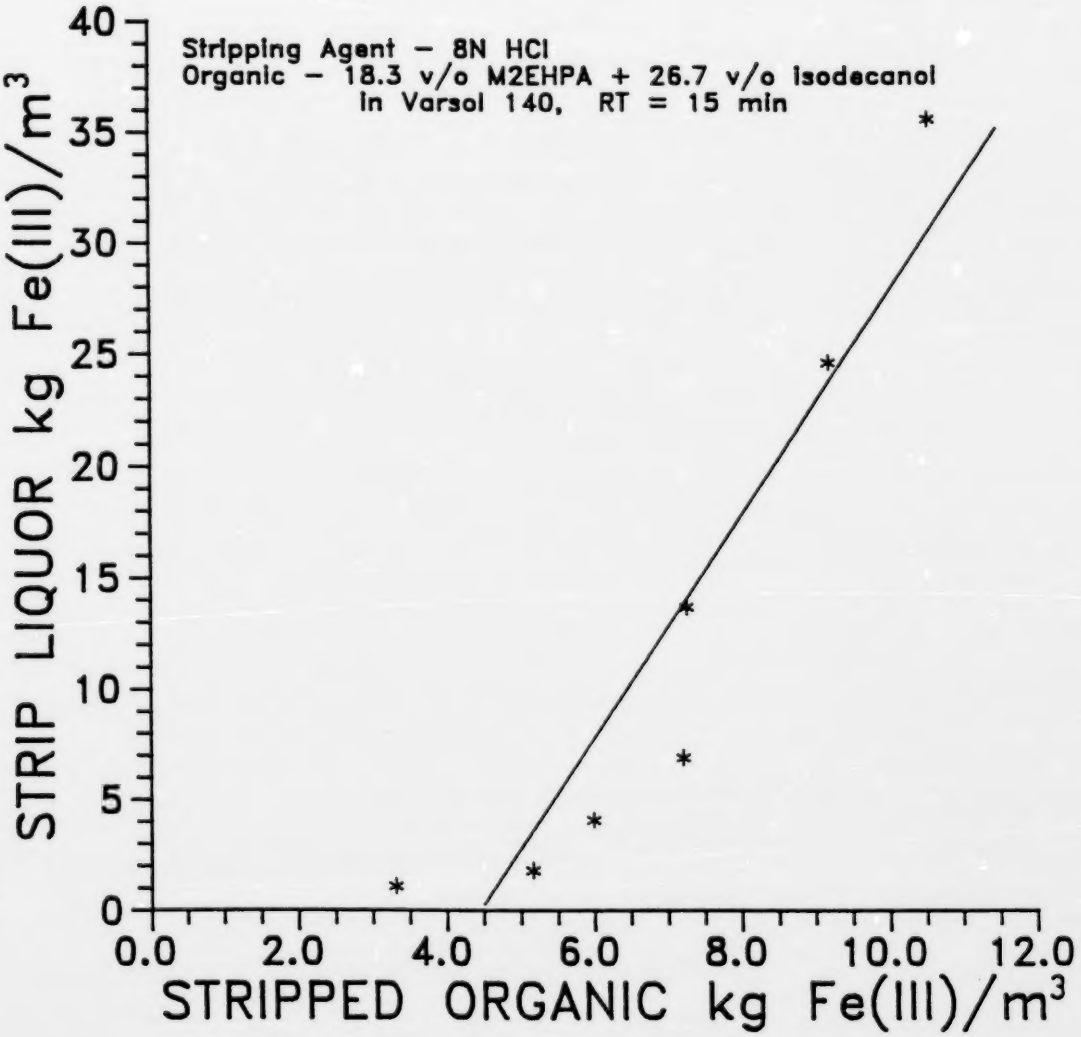


Fig. 3. Stripping isotherm of Fe(III)/M2EHPA/HCl

It appears that some Fe(III) remains in the stripped organic. This could be explained by the fact that under these acidic conditions (8 N HCl) the modifier (isodecanol) can be protonated and extract Fe(III) through an ion pair formation mechanism. This has been observed with Au(III) which forms the same type of complex with isodecanol, as Fe(III), at high HCl concentrations[2]. More research is necessary to optimize the stripping conditions.

CONCLUSIONS

From the above data it is concluded that M2EHPA is an excellent extractant for ferric iron from zinc electrolyte. Presently Noranda and six European companies are trying to develop this extraction system in order to purify their Zn electrolyte solutions.

REFERENCES

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